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Q16

Catalytic Oxidation of Hydrocarbons Using Iodosylbenzene in the Presence of a Ruthenium(III) Porphyrin Complex

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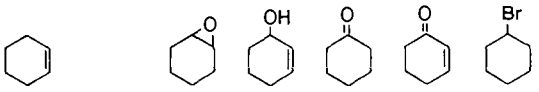
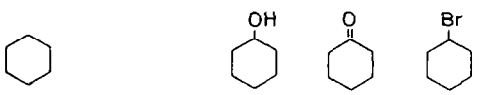
The ruthenium(III) octaethylporphyrin complex, Ru(OEP)(PPh_3)Br, *1*, has been prepared by the oxidation of Ru(OEP)(PPh_3)$_2$ [1] with excess bromine, and fully characterized by spectroscopic and crystallographic methods [2]. We have found that CH_2Cl_2 solutions of *1* (5×10^{-3} *M*) containing iodosylbenzene (0.1 *M*) catalyze at 20 °C the oxidation of certain olefins and cyclohexane (0.2–0.5 *M*). Some of the oxidation data are summarized in Table I.

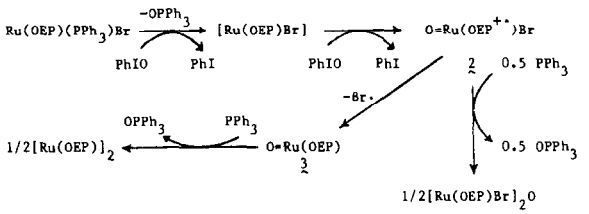
Groves *et al.* [3] have reported on corresponding oxidations using iron(III) porphyrins, and have presented evidence for involvement of an oxoiron(IV) porphyrin cation–radical intermediate, $O=Fe^{IV}(porp^{+\bullet})$. This is equivalent electronically to iron(III) plus the oxygen atom (from iodosylbenzene), and is overall at the same oxidation level as the active species in the cytochrome P-450 enzyme cycle; the enzyme systems utilize molecular O_2 for alkene epoxidation and hydrocarbon hydroxylation, and active $O=Fe^{IV}(porp^{+\bullet})$ intermediates have been implicated [3–5].

Studies with our ruthenium(III) system have led to isolation of closely related cation–radical species. Thus, reaction of *1* with PhIO yields a green complex tentatively formulated as $O=Ru^{IV}(OEP^{+\bullet})Br$, *2*. A strong ESR signal at g = 2.00 (at 77 K or 20 °C), and a broad Soret band at 384 nm coupled with bands at 502 and 604 nm, are typical of cation–radical species [1, 4]; a stoichiometric spectrophotometric titration with PPh_3 (complex *2*: PPh_3 = 2.0) to give quantitatively $OPPh_3$ and $[Ru^{IV}(OEP)Br]_2O$ [6] (see Scheme), and detection of bromine as cyclohexylbromide in the hydrocarbon oxidations (close to stoichiometric based on Ru, up to 85%, see Table) are consistent with the oxygen and bromine content of *2*, and with *2* being the active oxidizing species *via* free-radical reactions [1, 9, 10]:

TABLE I. Oxidation of Hydrocarbons with Iodosylbenzene Catalyzed by Ru(OEP)(PPh_3)Br.[a]

Substrate	Products	Yield[b]	Total turnover on metal
Styrene	Styrene oxide	21	10
Norbornene	Norbornene oxide	8	4
Cis-stilbene	Stilbene oxide	trace[c]	–
Trans-stilbene	(No reaction)		–
	(1 : 1·7 : 0·5 : 3·4 : 0)	3	1.5
	(1 : 1·5 : 0·3 : 0·3 : 0·3)[d]	12[d]	6[d]
	(1 : 8 : 9)	3.5[c]	1.7

[a]In CH_2Cl_2 at 20 °C after reaction time of 6 h. [b]Based on C_6H_5IO; this does not include loss of C_6H_5IO due to decomposition to PhI and $PhIO_2$ (~40% over 6 h). [c]As in *a*, but reaction time of 15 h. [d]In CH_3CN.



Scheme.

An inactive green complex, isolated at the end of the oxidations, and also formed by decomposition of *2* in solution, is believed to be a O=Ru(OEP) species, *3*, since it reacts quantitatively with PPh_3(1:1) to give the phosphine oxide and $[Ru(OEP)]_2$ [8]. Species *3*, which is rapidly converted by trace amounts of base into $[Ru(OEP)(OH)]_2O$ [7, 8], may contain an axial water ligand in which case it would resemble O=Ru(bipyridine)$_2$(py), which is known to oxidize PPh_3 by an oxygen atom transfer mechanism [11].

Spectroscopic studies are in progress in attempts to characterize more fully the putative oxo species *2* and *3*.

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Q17

Unusual Spin Interactions in the 24 Heme Hydroxylamine Oxidoreductase and Diheme Cytochrome *c* 554 from *Nitrosomonas*

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Nitrosomonas oxidizes NH_3 to HNO_2 with NH_2OH as an intermediate. Oxidation of NH_2OH appears to involve two multiheme cytochromes: hydroxylamine oxidoreductase (HAO) [1] and cytochrome *c* 554 [2]. Hemes of HAO have midpoint potentials varying from +100 mV to −350 mV [3]. HAO can accept electrons from NH_2OH and pass them to cyt *c* 554 (midpoint potential −50 mV, 2).

HAO, with an $\alpha_3\beta_3$ subunit structure, contains 7 *c*-type hemes and one unique heme P460 per $\alpha\beta$ dimer. The CO-binding heme P460 is essential for the NH_2OH dehydrogenase activity and is specifically destroyed by H_2O_2. EPR studies of HAO reveal several classes of low spin (s = ½) hemes [4]. Two species, accounting for half of the hemes, have been assigned g-values by reductive EPR titration; g = 3.06, 2.14, 1.35 and g = 2.98, 2.24, 1.44 [5]. Only four other EPR signals appear in the oxidized spectrum (g = 3.38, 2.70, 1.85 and 1.66). These resonances titrate coordinately but are not typical of magnetically isolated heme spectra. The apparent g-values of these 4 resonances are frequency dependent suggesting that they arise from spin-interactions of the hemes. Frequency dependence of the type observed has not been previously reported. The Mössbauer spectrum of ferric HAO contains a quadrupole doublet at 4.2 K in addition to the expected broad magnetically split spectrum, typical of s = ½ hemes. This doublet, which corresponds to at least one and probably two irons per $\alpha\beta$-dimer, has parameters (ΔE_Q = 2.1 mm/s and δ_{Fe} = 0.24 mm/s) which are typical of either low spin ferric heme with fast electronic spin relaxation or a pair of spin-coupled hemes [6]. We speculate that this doublet may be associated with the four frequency dependent EPR resonances. Heme P460 is not a component of the latter species since selective destruction of P460 by H_2O_2 fails to alter the EPR spectrum of the oxidized HAO. Thus heme P460 of native HAO is EPR silent.

Cytochrome c554 at pH 7 has an unusual 10 K EPR spectrum (g = 4.18, 3.85) similar to intermediate spin (s = 3/2) complexes. At pH 4 the EPR spectrum consists of one high spin (g = 6.0, 2.0 and one low spin (g = 2.93, 2.25, 1.52) component. At pH 2 a single high spin component (g = 6.0, 2.0) is present, whereas two low spin forms are observed at pH 10.5. Optical spectra of oxidized cyt *c* 554 at 20 °C are consistent with high spin heme at pH 4 and low spin heme at pH 10.5. Reduced cyt *c* 554 reacts with O_2 and binds CO at pH 4: the CO spectrum has two Soret maxima indicating a different interaction with each heme. ^{1}H-NMR spectra at room temperature show contact shifted heme methylene resonances in both the low spin (10–30 ppm) and high spin (60–100 ppm) Fe^{3+} spectral regions at all pH values between 4.5 and 9. Contact shifted resonances similar to those reported for s = 3/2 model heme complexes are not observed at this temperature. We conclude that the unusual low temperature EPR spectrum at